

JP2000-355885A (Corporation Kurare)

Title

Production process of artificial leather

Objective

To develop a production process of artificial leather, which offer equivalent quality to natural leather in terms of good feeling, soft touch, dyeing capability, long term weatherability with organic solvent free process.

Abstract

Back ground of invention

Artificial leathers made with non-woven fabric and PU resin as binder occupy very important position in the market place as an alternative substrate of natural leather. Particularly artificial leather based on a non-woven fabric fabricated with quite fine fiber offers high quality feeling. There are two processes in making artificial leather with fine fiber and PU resin.

i) A non-woven fabric is fabricated with a fine fiber made with co-spinning process of two different type fibers. After the non-woven fabric is soaked into PU resin, a part of fiber is removed with solvent or physical sizing process, and size of fibers is reduced.

ii) Non- woven fabrics made with fine fiber are treated with solvent or physical sizing to remove part of fiber to reduce the size of the fiber. After this pre-treatment, the non-woven fabric is soaked to PU resin.

In production process , there are two different types of process.

i) Polyurethane resin is dissolved into organic solvent such as DMF. Non-woven fabric is soaked into above PU resin solution, then the PU resin in fabric is coagulated in the water. (wet method) by dissolving DMF into water.

ii) Non-woven fabric was soaked into a solution or emulsion containing PU resin, after wring the excess resin out, the solvent or water in the fabric is dried off (dry method).

Artificial leather made with above wet process provide much more natural leather like feeling compared with drying process. However productivity is low and the use of DMF itself is an issue in terms of clean environment. On the other hand dry process eliminate the use of organic solvents such as DMF, but the feeling and touch of the leather made with drying process is not as good as that obtained with wet process. In drying process, PU resin strongly binds the fiber together, and the substrate feels hard. There are some cavities in the fabrics, where no PU resin penetrates consequently leather like feels can not be obtained.

In drying process based on PU water emulsion, an production process of artificial leather, which allows natural leather like soft touch, excellent dyeing capability, and excellent weatherability is strongly demanded.

Principle

Non woven fabric fabricated with fine fiber is soaked into PU emulsion complying with five requirements shown below and after curing by heat the size of the fiber constituting the fabric is reduced.

- 1) Heat gelable multiple emulsion
- 2) 100 micron film made with this emulsion by drying at 50 deg C provides modulus less than 5.0×10^8 dyn/cm² at 90 deg C.
- 3) 100-micron film made with this multiple emulsion by drying at 50 deg C provides modulus greater than 5×10^6 dyn/cm² at 160 deg C.
- 4) Multiple emulsion, where ethylenic unsaturated monomer(B) is reacted under PU emulsion(A) in the ratio of A:B= 70:30-10:90
- 5) In this multiple emulsion contains 0.1-50mmol of t- amine against 100g of this multiple emulsion.

Experimental session

Heat gelation temperature

10g of emulsion was charged to a test tube. The test tube is subjected to a water bath of 90 deg C. The emulsion was heated up while agitating. The temperature when the emulsion gelled was measured as heat gelation temperature.

Modulus and alpha dispersion temperature

100 micron thick film was prepared with the emulsion by drying up at 50 deg C. The film was heat treated at 130 deg C for 10 min. Modulus (E) at 90 deg C and 160 deg C respectively and alpha dispersion temperature (T alpha) were measure with a ET REO Spectrometer DVE-V4.

Softness of synthetic leather (Flexural modulus)

Synthetic leather of 10 x 10cm² are subjected to testing of flexural modulus at 20 deg C and 65% RH. The sample was taken perpendicular direction against the direction of rolling out the leather.

Bending test

The sample of the synthetic leather, 7cm x 4.5cm was subjected to a bending test. The sample was bent according to a JIS K 6545 at 20 deg C and 65% RH. The sample was inspected every 100000 times, and the sample showing no crack or no hole until 500000 times was acceptable for durability.

Touch of the synthetic leather

The surface of synthetic leather was inspected by hand. If the touch is soft feel like natural leather, the touch is acceptable. If the feeling is coarse and hard, a touch is un -acceptable.

Dying of synthetic leather

Surface of the synthetic leather was fuzz by a sandpaper, and was subjected to dyeing process in a mixture of Chiba Gygi metal containing dye (acid type dye) and water (1:4) at 90 deg C for 1 hrs. If the leather has uniform dying, it is acceptable. Uneven dying on the leather is judged as unacceptable.

UV weatherability of the dy d leather

The died leather was subjected to UV weatherability test according to JIS L 0804 test method, where carbon ark lump was used as light source. The degree of color fading was inspected.

Raw material used for preparation of mulsi n

PMPA 2000: 2000mw polyester diol made with 3-methyl-1,5 pentane diol and adipic acid

PTMG: 1000mw-poly tetra methylene glycol

PHC 2000: 2000mw poly hexa methylene carbonate diol.

Reference-1 (Preparation of non woven fabric)

60 pph of 6-nylon and 40pph of high flow polyethylene are subjected to co-spinning process following drawing and cutting. Fibers of 4 diner x 51mm are fabricated to non-woven fabric of 0.16g/cm³ density. The fabric was heated and the polyethylene was partially melted as a binder to put the fiber together. Then, a fabric of 0.285g/cm³ density having flat surface was obtained.

Reference-2 (Preparation of polyurethane emulsion)

300g of PMPA 2000, 60.87g of 2,4 toluene di-isocyanate, 7.85 g of 2-bis (hydroxy propionic acid are charged to a three neck flask. The mixture was reacted at 90 deg C for 2 hrs, and isocyanate-terminated pre-polymer was obtained. 195.4 g of 2-butanon was blended to above pre-polymer, and the temperature was reduced to 40 deg C. Then, 5.92 g of tri-ethyl amine was added to above pre-polymer, and was agitated for another 10 min. This pre-polymer was blended with a mixture of 7.83g of sodium lauryl sulfate and 285.0g of water, and was agitated for 1 min with a homogenizer. Immediately after the agitation, a mixture of 6.91 of di-ethylene tri-amine and 5.70g of Isophorone di-amine and 496.4g of water was added to above emulsion. The mixture was agitated for another 1 min and chain reaction was completed. 2-butanon was removed from above emulsion by evaporation, and **PU-Emulsion-1** having 35% solid was obtained.

Reference-3 (Preparation of polyurethane emulsion)

150g of PTMG 1000, 150g of PHC 2000 and 74.45 of toluene di-isocyanate, and 9.05g of 2,2 bis (hydroxymethyl) propionic acid were charged to three neck flask. The mixture was heated at 90 deg C for 2 hrs under nitrogen atmosphere, and NCO terminated pre-polymer was obtained. 20.9g of 2-butanon was added to this pre-polymer. After agitation, 6.83 tri-ethyl amine was added, and was agitated for another 10 min. A mixture of 6.1g of sodium lauryl sulfate (anionic surfactant, ETX-3NEX) and 296.6 g of water was added to above pre-polymer, and was agitated for 1 min with a homo-mixer. Immediately after agitation, a mixture consisting of 6.62g of di-ethylene tri-amine, 1.93g of ethylene di-amine and 514.8g of water was added. The mixture was agitated for another 1 min, and 2-butanon was removed by evaporation, and **PU Emulsion-2** of 35% solid was prepared.

Reference-4 (Preparation of polyurethane emulsion)

PU emulsion-3 having 35% solid was prepared according to a procedure written in reference 2 except for one change, where 4.87g of n-methyl-3,3' imino bis-(propylamine) was used instead of Isophorone diamine. The emulsion obtained was named **PU emulsion-3**

Example-1 (Preparation of artificial leather)

(1) Preparation of multiple dispersion

(i) Preparation of multiple emulsion

240g of PU emulsion-1 obtained in Reference –2, 0.02g of FeSO₄, 7 H₂O, 0.294g of potassium pyrophosphate, 0.451 of rongalite, 0.020 g of EDTA, .2 Na and 246g of water were charged to a three neck flask having a condenser. The mixture was heated up to 40

deg C under nitrogen atmosphere.

(ii) A mixture-1 of 147.4g of butyl acrylate, 4.70g di-ethyl amino ethyl methacrylate, 3.14g of 1,6 hexane diol di-acrylate, 1.57g of aryl methacrylate, and the emulsifier (ECT-3NEX) (a mixture of 1.57g of monomer mixture, 0.14g of cumene hydro peroxide, 0.314g of ECT-3NEX and 15g of water) were dropped to a flask for 4 hrs through a dropping funnel. Then, the mixture was heated at 40 deg C for 30 min.

(iii) A mixture consisting of 38.4 g of methyl methacrylate, 0.78g of 1,6 –hexane diol di-acrylate and 0.392 of ECT-3NEX, and a mixture consisting of 0.078g of cumene hydro peroxide, 0.078g of ECT-3NEX and 3.0g of water was charged to above emulsion made in (ii) through different dropping funnel for 90 min. After addition, the mixture was heated for 60 min and polymerization was completed. Thus, an emulsion having 40% solid was prepared.

(iv) 4 pph of EMULGEN 109P (nonionic surfactant) and 1 pph of calcium chloride are blended to 100 pph of multiple emulsion obtained in (iii), and a heat gelable PU emulsion was obtained.

Gel temperature of this emulsion, Modulus of the film prepared with this emulsion at 90 deg C and 160 deg C, and alpha dispersion temperature(T_{α}) of the film are shown in Table 4 respectively.

(2) Preparation of synthetic leather

i) Non woven fabric made at a procedure in reference-1 is soaked to the heat gelable emulsion prepared in Example -1. The fabric was squeezed with a press role and was dipped in the water of 90 deg C for 1 min following drying at 130 deg C for 30 min. Thus, artificial leather was prepared.

ii) Above artificial leather prepared in (2),i) was dipped in a toluene of 90 deg C the leather was squeezed with a press role of 2kg/cm² five times and polyethylene fiber was dissolved. The PU resin content of the total leather weight was 60%. Modulus, bending test data, touch (feeling), dyeing capability, weatherability is summarized in table 4. This artificial leather offered excellent touch like natural leather, and weatherability and dying ability were excellent.

Example-2 (Preparation of artificial leather)

1. Preparation of multiple emulsion

Multiple heat gelable PU emulsion was prepared according to a procedure described in Example 1 with a component shown below (table 1). Gel temperature, Modulus E of the film at 90 deg C and 160 deg C and alpha dispersion temperature are shown in table 4.

2. Preparation of artificial leather

i) Non woven fabric obtained in reference-1 was soaked into the emulsion prepared with the procedure described in Example-1. After squeezing the excess resin, steam of 1.5kg/cm², 112 deg C, was applied to the fabric containing PU emulsion following drying up in an oven of 130 deg C for 30 min. artificial leather was prepared.

(ii) The fiber in non-woven fabric was down sized by dissolving polyethylene fiber according to a procedure in (ii) of (2) in Example- 1. Weight of PU resin in the leather was 59 wt %.

Modulus, bending test data, touch, dyeing ability and weatherability of the leather obtained are summarized in table 4. All performance was excellent just like natural leather.

Table-1

PU: polyurethane
BA: buthyl aclyrate
EHA: 2-ethyl hexyl acrylate
MMA : Methyl metacrylate
DMAEMA: di-methyl amino ethyl matacrylate
DEAEMA : di-ethyl amino ethyl metacrylate
R-HALS : 4- metactyl oxi-1,2,2,6,6-penta-methyl pyperidine.
HDDA : 1,6-hexan diol di acrylate
ALMA: arylmetacrylate
St: styrene
ECT-3NEX: anionic surfactant
CHP: cumen hydroperoxide

Table 2

Example –3 (Preparation of artificial leather)

(1) Preparation of multiple emulsion

Heat gelable multiple emulsion was prepared according to a procedure of (1) in Example-1, with a component in table 2. The data obtained are summarized in table 4.

Table -4

(2) Preparation of artificial leather

- (i) 0.5 pph of wetting agent, POLYFLOW KL 260, was added to 100 pph of above emulsion prepared with a procedure (1) in Example 3. Then, non-woven fabric obtained in a procedure described in reference-1 was soaked to this emulsion. After squeezing, and heating at 130 deg C for 30 min, artificial leather was obtained.
- (ii) The fiber in non-woven fabric of above artificial leather,(i) of (2) was downsized by dissolving polyethylene fiber by toluene in according to a process in section (ii) of (2) in Example-1. PU resin content of this artificial leather was 54%. The data tested for this leather are summarized in table -4. All performance was excellent

Example-4 (Preparation of artificial leather)

(1) Preparation of synthetic leather

Heat gelable multiple emulsion was prepared according to a procedure in (1) of Example – 1 with component in table 2. The test data for the film made with dispersion are summarized in table 4.

(2) Preparation of synthetic leather

Non woven fabric prepared according to a procedure in reference-1 were soaked to the emulsion obtained in above procedure. The PU resin content of the artificial leather was 71% after downsizing of the fiber. The test data for this artificial leather are summarized in table 4. All performance was excellent.

Comparison test-1 (Preparation of artificial leather)

(1) Preparation of multiple emulsion

(i) 240g of PU emulsion-2 obtained in reference –3, 0.020g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.294g of sodium pyrophosphate, 0.451g of rongalite, 0.020g of EDTA, 2Na and 244g of water were charged to three neck flask, and was heated up to 40 deg C under nitrogen atmosphere.

(ii) 180.3g of methyl methacrylate, 5.88 g of diethyl amino ethyl methacrylate, 9.8 g of 1,6-hexane diol di-acrylate and 1.96g of anionic emulsifier(ECT-3NEX) mixture used in reference-3 and a emulsifier consisting of 0.392g of cumene hydro peroxide, 0.392g of emulsifier (ETC-3NEX) and 20.0pph water are added to above mixture through separate dropping funnel for 5 hrs. After addition, the polymerization was completed at 50 deg C for 60 min, and emulsion of 40% solid was prepared.

(iii) 100pph of above multiple emulsion prepared in (ii) were mixed together with 4 pph of nonionic surfactant, EMULGEN 109P, and 1 pph of calcium chloride. Thus, heat gelable PU emulsion was obtained. The gelation temperature of this heat gelable multiple emulsion, modulus of the film made with this emulsion at 90 deg C and 160 deg C, and alpha dispersion temperature are shown in table 5.

Table 5

(2) Preparation of artificial leather

Non woven fabric made according to the procedure in reference-1 was soaked into PU emulsion prepared according to above procedure, Reference-1 (1). After downsizing of the fiber, artificial leather was prepared. The PU resin content of the leather was 58%. Testing data obtained for this leather are summarized in Table 5. All performance was not acceptable.

Comparison test 2 (Preparation of synthetic leather)

(1) Preparation of multiple emulsion

A heat gelable multiple emulsion was prepared according to a procedure written in

comparison test-1 but with component listed in Table-3. The gelation temperature and polymer properties of the film made with this emulsion are summarized in table-5.

Table-3

(2) Preparation of artificial leather

Non woven fabric prepared with a reference-1 are soaked into the emulsion prepared in above procedure. After down sizing of the fiber, artificial leather was prepared. The resin content in the leather was 57%. Properties of this leather are summarized in table-5. The leather showed paper like feeling and the tough of this leather was not acceptable.

Comparison test-3(Preparation of synthetic leather)

(1) Preparation of multiple emulsion

A multiple emulsion was prepared according to a procedure in Example-1, (1), (i) to (iii) without gel promoting agent (EMULGEN109P and calcium chloride). This emulsion did not show heat gelable characteristic. Polymer physicals of the film obtained are summarized in table 5.

(2) Preparation of synthetic leather

Non woven fabric made with a procedure in reference-1 was soaked in the emulsion prepared in above procedure. Then, it was treated in hot water, but the emulsion bled into the water. The fiber of the non-woven fabric was downsized according to a procedure in Example -1, (2),(ii). The PU resin content of the leather was 32 wt %. Physicals are summarized in table 5. The leather showed paper like touch, and all performance was un acceptable.

Comparison test-4(Preparation of synthetic leather)

(1) Preparation of multiple emulsion

Heat gelable polyurethane emulsion was prepared according to the procedure in (1) of Example -1 with components in table 3. The physical data obtained for this heat gelable emulsion and a film made with this emulsion by drying up are summarized in Table-5.

(2) Preparation of synthetic leather

Non woven fabric prepared according to a procedure in reference-1 was soaked into above heat gelable emulsion. After size reduction of the fiber consisting non-woven fabric, a artificial leather was prepared. The PU resin content of the synthetic leather was 55%. The physicals of the leather are summarized in Table 5

Summary

As shown in example 1 to 4, non woven fabric made with fine fiber soaked into heat gelable emulsion complying with requirements 1-4 in the section “**Principle**” showed natural leather like high quality feel. Dyeing ability, weatherability, and fatigue of those leather were

all excellent.

However, as shown in reference –1 in table- 5, the film made with the emulsion in reference –1 has modulus of 6.9×10^8 dyn/cm², and does not comply with the requirement –2 in a section “**Principle**”. Artificial leather made with this emulsion showed hard feel and coarse touch.

As shown in reference-2 in table-5, the film made with multiple emulsion showed 3.9×10^6 dyn/cm² at 160 deg C, and did not comply with requirement-3 in the section “**Principle**”. The artificial leather made with this emulsion gave high modulus and coarse touch, and was not acceptable.

As shown in reference-5 of Table-5, artificial leather made with a non-heat gelable multiple emulsion, which does not comply with requirement-1 in a section “ **Principle**”, gave high modulus. The leather did not show natural leather like soft touch.

As shown in reference-4 of Table-5, artificial leather don't offer adequate dyeing capability and UV stability when multiple emulsion does not contain t-amine group.

Claim

Claim-1

This invention claims a production process of artificial leather made with a non-woven fabric fabricated with fine fiber and multiple emulsion complying with item 1 to 5 shown below, where the fabric is soaked into the emulsion first and coagulated second by heating, then the fiber consisting the fabric is down sized.

1. Heat gelable multiple emulsion
2. 100-micron films made with this heat gelable multiple emulsion by drying at 50 deg C provide modulus of less than 5×10^8 dyn/cm² at 90 deg C.
3. 100-micron films made with this heat gelable multiple emulsion by drying at 50 deg C provide modulus of greater than 5.0×10^6 dyn/cm² at 160 deg C.
4. Ethylenic unsaturated monomer B is polymerized in the PU emulsion A in the ratio of PU emulsion A: ethylenic monomer B/ 70:30-10:90)
5. This multiple emulsion contains 0.1-50 mmole of t-amine group in 100g of this emulsion.

Claim-2

Production process, where fine polyamide fiber is one of the components constituting the non-woven fabric.

Claim-3

Production method, where 100 micron film made with this emulsion in claim-1 or claim-2 by drying at 50 deg C provide alpha dispersion temperature of below –10 deg C.

Claim-4

Production process in claim-1 to claim-3, where PU emulsions (A) are based on aromatic poly isocyanate.

Claim-5

Production process in one of claim-1 to claim-4, where ethylenic unsaturated monomer (B) is either (meta)-acrylic acid and/or a mono functional ethylenic monomer (B1) derived from (meta)-acrylic acid, 90-99.9 wt % and multi functional ethylenic monomer (B2), greater then two functional, 0.1-10 wt %.

Claim-6

Production process in one of claim 1 -5, where ethylenic monomer(B) contains 0.1-10 wt % of t-amine group

Claim-7

Production process in one of claim 1-6, where fine fiber is made with co spinning process with two different types of fibers. The fiber is fabricated to a non woven fabric, and the fabric is soaked into PU emulsion first and is dried by heating. After above process the fiber is down sized by removing one of tow fibers.

Claim-8

Production process in one of claim 1 to 7, where gelation temperature of the heat gelable multiple emulsion is 30 to 70 deg C, and the emulsion is soaked into fabric and is coagulated by heating at higher temperature than gel temperature by 10 deg C.

Claim-9

Artificial leather prepared with a process one of the claim 1 to 8.